

DNA Metallization Processes and Nanoelectronics

Arianna Filoramo

Abstract DNA fascinates for its exceptional assembling properties which make it an ideal candidate to encode instructions for nano-scale assembly. However, to utilize DNA not only as a positioning scaffold but also for electrical interconnections, it is pragmatically envisioned to metallize it. Here, an overview of DNA metallization processes is presented.

1 Introduction

The Silicon-CMOS technology is the base of present hardware technology for information processing. Until now, its evolution is governed by Moore's laws (1970s), stating that microprocessor performance (defined as the number of transistors on a chip) doubles every 18 months. However, even if no doubt is raised for its future use and deployment, the International Technology Roadmap for Semiconductors (ITRS) [1] still predicts that the present CMOS technology will benefit by the contribution of complementary approach and emerging material and devices.

This motivates the research community to study and develop alternative nanofabrication technologies, which could possibly enable the production and manipulation of well-defined structures at the nanoscale level. Indeed, it is undeniable that conventional technologies based on "top-down" approaches are foreseen to experiment difficulties. At this scale, self-assembly, and more generally, "bottom-up" approaches appear to be a reasonable way to assemble nano-objects into circuits with a two-dimensional and/or three-dimensional layout. In particular, self-assembly is also identified as the one promising way to reduce significantly the fabrication costs compared to what is expected for standard top-down silicon-based

A. Filoramo (✉)

Laboratoire d'Electronique Moléculaire, Service de Physique de l'Etat Condensé,
IRAMIS/DSM/CEA, CEA Saclay, 91191 Gif sur Yvette, France
e-mail: arianna.filoramo@cea.fr

devices. Indeed, the basic idea of self-assembly is to use a process involving the spontaneous self-ordering of substructures into superstructures. This spontaneous self-ordering is due to specific chemical or physical properties of matter, and relies on the natural tendency of the system to search for a stable configuration.

Among the new methodologies based on bottom-up approaches for future nanotechnology, the exploration of the bio-directed assembly for organizing nano-objects is one of the most promising ones. Indeed, the nanoscale is the natural scale on which biological systems build up their structural elements, and biological molecules have already shown great potential in the fabrication and construction of nanostructures and devices. In this context, the DNA molecule is of particular interest, as highlighted by the increasing number of recent works devoted to the study of its physical properties and implementation in nano-constructions and nano-electronics. Indeed, the DNA molecule has already been successfully used to build up nanostructures [2, 3] or scaffolds for nanoparticles' assembly [4–7]. Moreover, one can envision its use for the assembly of devices [8]. The key advantage in using DNA as a scaffold for these constructions is that its intra- and inter-molecular interactions are the most readily known, easily engineered, and reliably predicted. Note that in this approach the genetic value of DNA is completely disregarded; only its structure and self-assembly properties are considered. The information contained in DNA sequences can be envisioned to code: (i) the assembly of the scaffold, (ii) its selective attachment on the surface microscale electrodes, (iii) the positioning of nano-objects or nanodevices on the scaffold and (iv) the realization of electrical connections and circuitry.

Here, we do not mean to present an exhaustive review of DNA-directed assembly techniques, but rather a focused discussion onto DNA metallization.

2 Why Is It Necessary to Metallize DNA?

The transport properties of DNA molecules have recently generated heated debate among scientists, as evidence both for and against the hypothesis of DNA as a conducting wire has been piled up. While no full consensus is completely reached yet, the extensive transport measurements carried out on single DNA molecules and DNA bundles strongly suggest that DNA in the dry state deposited on a substrate is a good insulator [9–12] and thus not useful as a conducting element. We believe that in spite of its somehow negative sense, such a conclusive statement is of great importance in defining strategies for implementing a DNA-based technology. Indeed, it becomes now clear that to achieve an electrical connecting use of DNA strands, it is necessary to proceed to their metallization. During the past 10 years, we have seen the rise of numerous methods to metallize DNA scaffolds and we will summarize in the following the main aspects and results.

3 The DNA Metallization Process

The feasibility of this biotemplating approach was firstly shown by Braun et al. [13]. The authors first immobilized a dsDNA strand between two electrodes. Then, they treated it with silver ions in order to perform an Ag^+/Na^+ ion-exchange and replace the natural sodium counter ions of the dsDNA backbone with silver ones. Successively, these silver ions were subjected to a chemical reduction process by hydroquinone (reducing agent) to form small silver aggregates. Finally, the silver nanoclusters fixed on the dsDNA strand were autocatalytically grown (using an acidic solution of hydroquinone and silver ions) to give a granular (100-nm width) nanowire contacting the two electrodes.

The majority of dsDNA metallization processes follows the same principle and can be decoupled in terms of successive steps, as schematically shown in Fig. 1 and discussed below.

The first step consists in biomolecule activation: the metal ions or metal complexes bind to dsDNA (Fig. 1a). The activation can take place by ion exchange mechanism (such as discussed above for silver [13]) on the DNA backbone or by insertion of the metal complexes between the DNA bases (like platinum or palladium complexes [14]).

In the second step, the bound metal ions or metal complexes are usually treated with a reducing agent (Fig. 1b). This converts them in metal nanoclusters fixed on the DNA strand. The more used reducing agents are dimethylaminoborane [15, 16], hydroquinone [13], and sodium borohydride [17]. An interesting variant has been proposed by Keren et al. [18, 19], who fixed the reducing agent (glutaraldehyde) directly onto the dsDNA strand in order to enhance specificity and reduce parasitic unwanted background metallization.

The key point is that at the end of these two steps, the dsDNA strand has some small metal nanoclusters fixed on it (as represented in Fig. 1c), which will successively act as “seeds” for the metallization of the DNA molecules.

The third step of the metallization process consists in autocatalytic growth of the fixed metal seeds on the DNA strand (Fig. 1d) by the addition of new metal ions (or metal complexes solution) and new reducing agent solution.

The principle of this autocatalytic process is that metal complexes or ions from solution are preferably reduced on already reduced metal nanoclusters (the seeds) fixed on the DNA strands. Here, it should be noted that this autocatalytic cluster growth can be generalized to metal nanoclusters fixed on DNA strand by any other method. Indeed, an effective metallization has been reported on ex situ prepared gold nanoclusters successively fixed on the dsDNA (i) by an appropriate chemical functionalization [21], (ii) by specially modified DNA construction [22], or (iii) simply by electrostatic interactions [23–25]. In this context, it is worth to quote the work of the Carell group on insertion in dsDNA sequence of modified bases to perform base-selective chemistry to conjugate metallic seeds. By this method, they inserted silver [26–28] or gold nanoclusters [29] selectively in the dsDNA

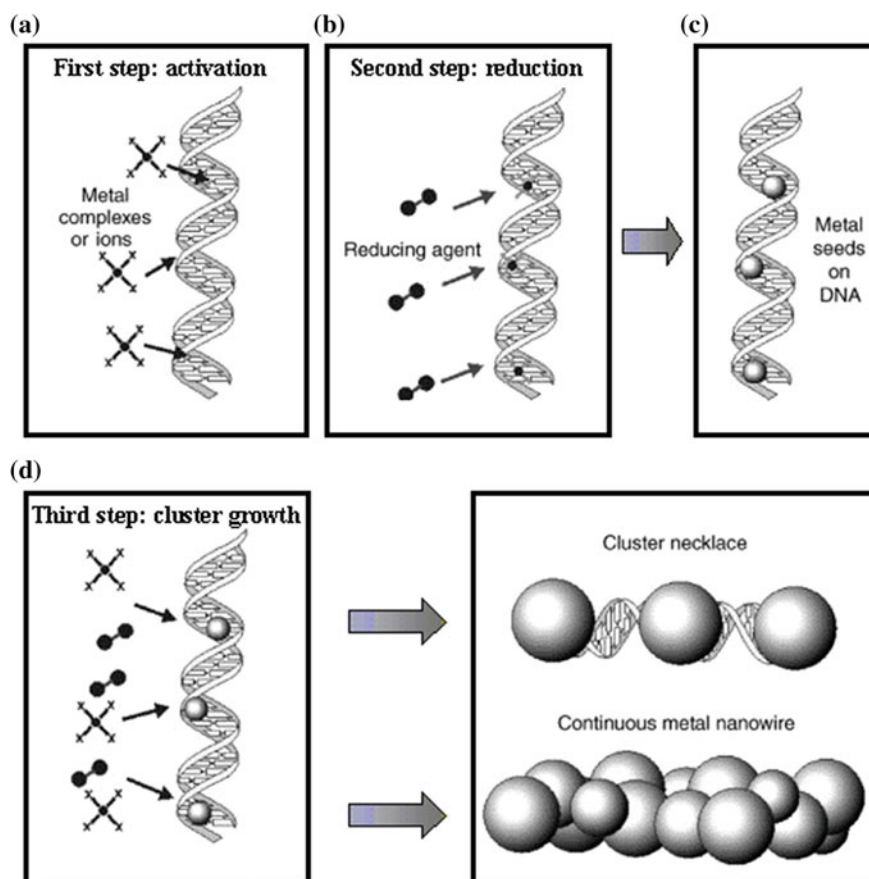


Fig. 1 Schematic representation of the different steps of the DNA metallization process. Adapted from Ref. [20]

sequence, then an electroless plating process (goldenhance) [30, 31] on such nanoclusters has been performed.

As mentioned above, different metals have been used in the metallization process. For the ion-exchange mechanisms on the dsDNA backbone, we can quote silver [13, 32], copper [33], or gold [34]. For the silver process, the obtained wires consisted in a chain of contiguous 30–50-nm Ag grains along the dsDNA backbone and the electrical measurements performed on such Ag necklace wires were not completely satisfactory. In a successive work, the same group improved the process by replacing the silver clusters growth with an electroless gold coating of the silver-loaded dsDNA molecules [19]. In this way, using silver ions as catalysts, conductive gold dsDNA-templated wires with widths ranging from 50 to 100 nm were obtained. This procedure can be generalized and the final metal coating does not necessarily have to use the same metal as the seeding one [19, 21, 35].

Concerning the intercalation mechanism of metal complexes between the DNA bases, the Pd or Pt complexes have been the more extensively studied. Indeed, the binding process of Pt(II) complexes to DNA is well investigated in the case of cisplatin (*cis*-[Pt(NH₃)₂Cl₂]), which is widely used as an anticancer drug [36]. It follows from these studies that when DNA is incubated with Pt(II) complexes such as cisplatin, the Pt(II) atom binds to one- or two-stacked DNA bases forming monofunctional and bifunctional DNA-Pt(II) adducts, respectively. The most favorable binding site for cisplatin to the DNA is the N₇ position of guanine, followed by the N₇ position of adenine [37, 38]. Indeed, the bases A, G, and C have exocyclic amine groups as well as ring amines, but it is the ring amines that act as Lewis bases. The Lewis base acidities differ from base to base, with the N₇ position of guanosine being the most basic. Other Lewis bases found in the nucleobases are N₇ of adenosine, N₃ of cytosine, and the deprotonated N₃ of thymidine or uridine. The amines are all soft ligands and as such preferably complex to soft metals such as Pt(II), Pd(II), or Ru(II). When the DNA is in double-strand configuration, the arrangement of the basis is controlled by π stacking and then the Lewis base sites available for coordination to the metal (Pd, Pt, etc.) are limited to the exposed portion of the nucleobases found in the major groove (the N₇ position of guanosine and adenosine). It is commonly thought that of these two sites, the N₇ of guanosine is the preferred one [38]. After these sites are occupied, the binding reaction proceeds more slowly and indiscriminately with other metal-binding sites of all bases [38–40]. Using this intercalation mechanism, Pd- and Pt dsDNA-coated nanowires have been obtained.

Finally, as an alternative way to DNA metallization, the photo-induced autocatalytic silver reduction has been reported [41]. The incident UV light with a wavelength near to the absorption maximum of the DNA bases (254 nm) induces the in situ reduction of silver ions that were preloaded onto the DNA samples. The bases act as light sensitizers for the Ag⁺ and thereby induce the formation of metallic silver clusters along the DNA strands.

A global schematic view of the main works reported in the literature is presented in Fig. 2. Note that the conductivity of the obtained nanowires has not been measured in all reports. Generally speaking, these metallization processes of the DNA strands have been performed either (i) in solution and then the metallized DNA molecule is deposited on the substrate for the characterization purpose, or (ii) on the DNA previously deposited on the substrate.

The first case concerns, for example, the works reported by Harnack et al. [21] and Mertig et al. [42], who showed the formation of tiny platinum nanocluster necklaces consisting of well-separated clusters of 3–5-nm diameter with spacing from one to several nanometers.

On the contrary, Richter et al. [43], Nguyen et al. [44], Deng et al. [45], Dupraz et al. [35], and Ongaro et al. [23] have metallized DNA strands already deposited on the substrate. More in detail, Richter et al. fabricated continuous Pd nanowires with average diameters of 60–100 nm on DNA strands aligned on interdigitated gold electrodes with interesting transport properties, while Nguyen et al. [44] obtained conductive Pd nanowires with diameters in the range of 30–60 nm. On the contrary,

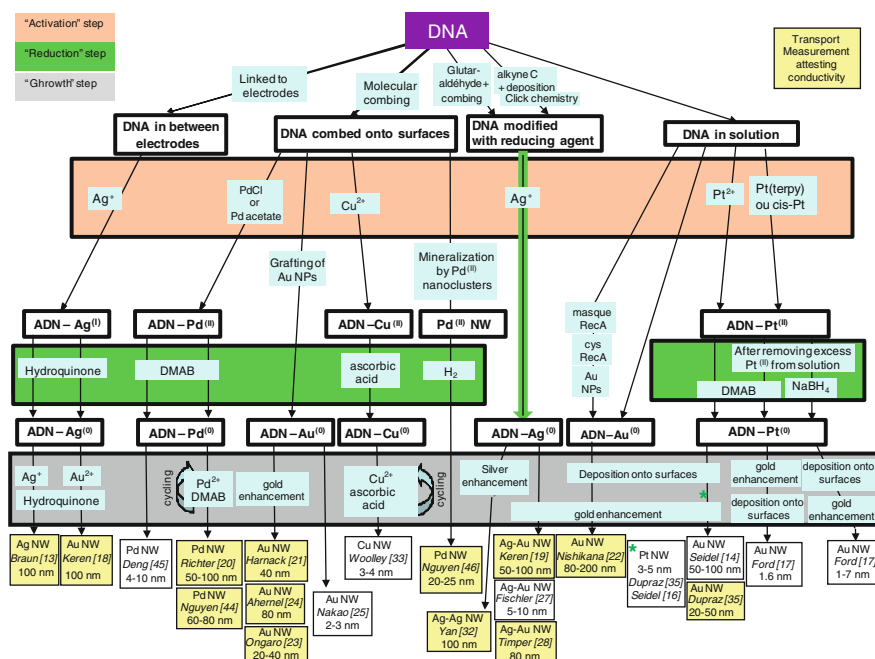


Fig. 2 Schematic representation of the main different pathways of the DNA metallization process. The yellow boxes represent the works where transport measurement has been performed

Deng and coworkers [45] reported very granular 30-nm Pd nanowires without any data about their conduction properties. Actually, both Dupraz et al. [35] and Ongaro et al. [23] started the metallization process in solution (seeds fixation) and successively stretched the metal-loaded DNA on the substrate. They used, respectively, Pt and gold nanoparticles as catalytic seeds, then they completed the metallization process by an Au electroless plating process. They both obtained DNA-templated Au nanowires (average diameters about 50 nm) with estimated resistivity of the order between 10^{-5} and $10^{-4} \Omega \cdot \text{m}$. At the time of writing, the thinnest conductive nanowires are about 20–25 nm in diameter [46].

At this point of our discussion, we should point out that among all the above-presented methods, only a few could be effectively and promisingly envisioned for nanocircuits' application. Indeed, the first condition that must be satisfied is that the obtained nanowires demonstrate good conducting behaviors. Then, as already noted, the metallization should be envisioned as the very last step of nanocircuits' fabrication since after this process all the recognition properties of the DNA molecules are completely lost. Finally, it is also crucial to be able to perform both effective and sequence-selective metallization where some parts of DNA scaffolds are not metallized (to avoid undesired electrical connections and shortcuts).

4 Sequence-Selective DNA Metallization

As mentioned above, in some cases, it can be desirable to define the parts of DNA strands to be metallized, while other parts are preserved. On this topic, we can quote three main studies which have been reported in the literature [18, 19, 22]. They are all based on the RecA protein properties. In vivo, the RecA protein is a central

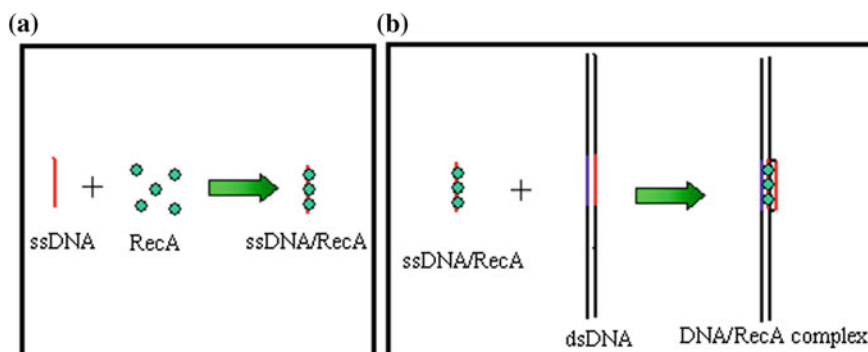


Fig. 3 Schematic representation of homologous recombination process that leads to binding of the ssDNA–RecA nucleoprotein filament at the complementary address on the dsDNA

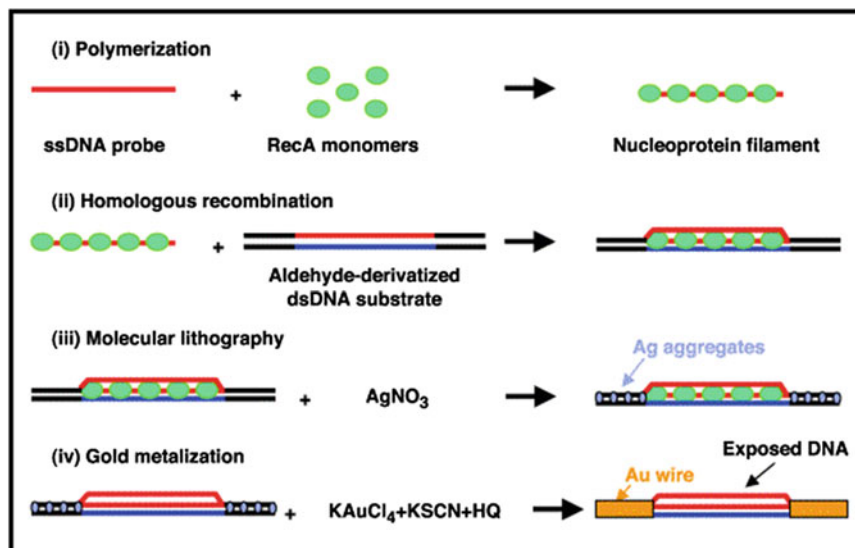
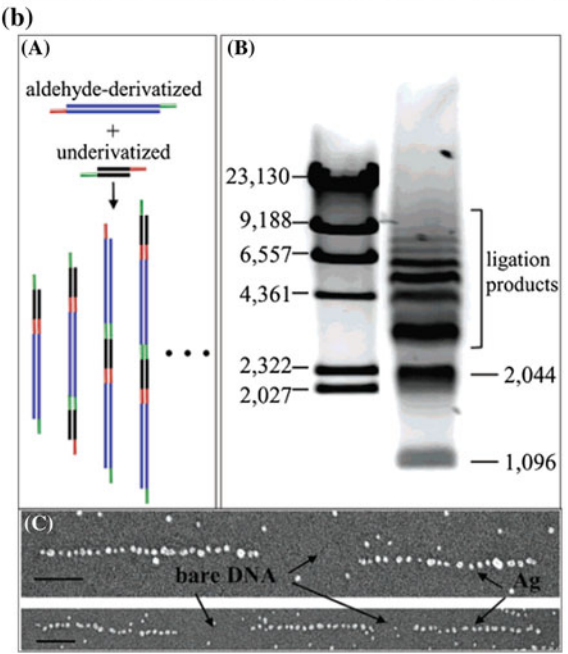
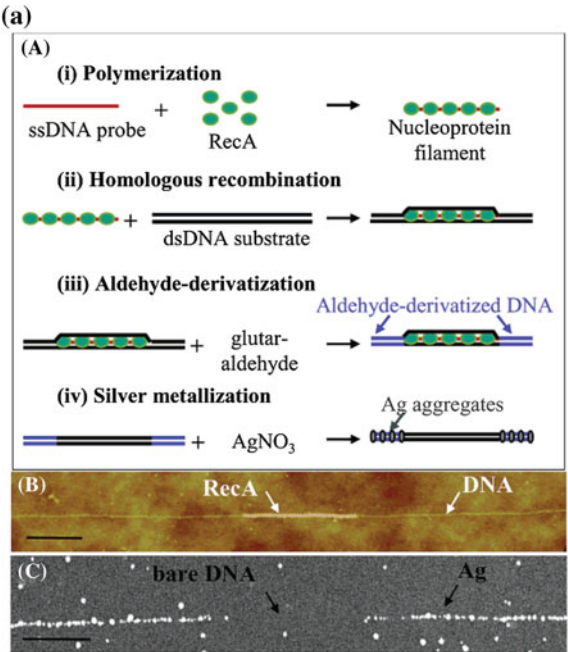


Fig. 4 Mechanism of sequence-selective metallization process. Thanks to the homologous recombination, the RecA protein acts as a sequence-specific resist for the creation of the silver seeds and successive gold metallization. From Ref. [18]



◀ **Fig. 5** **a** Selective metallization obtained by protection against aldehyde-derivatization of DNA using RecA as a sequence-specific resist. (A) Schematics of the protection reaction. (i) RecA monomers polymerize on a ssDNA probe molecule to form a nucleoprotein filament. (ii) The nucleoprotein filament binds to a dsDNA molecule at a homologous sequence. (iii) Incubation with glutaraldehyde leads to aldehyde derivatization of the substrate molecule in regions unprotected by RecA. (iv) Incubation of the patterned substrate DNA molecules in silver solution results in the formation of silver clusters in the aldehyde-derivatized regions, while the underivatized protected regions remain bare. **b** Selective metallization obtained by ligation of aldehyde-derivatized and -underivatized DNA fragments. (A) Schematic illustration of the ligation reaction (B) Gel electrophoresis analysis of the ligation reaction (*right lane*) run against a *λ*-HindIII digest marker (*left lane*). (C) SEM images of patterned metallization of DNA molecules obtained by ligation of alternating aldehyde-derivatized fragments and -underivatized ones. Adapted from [19]

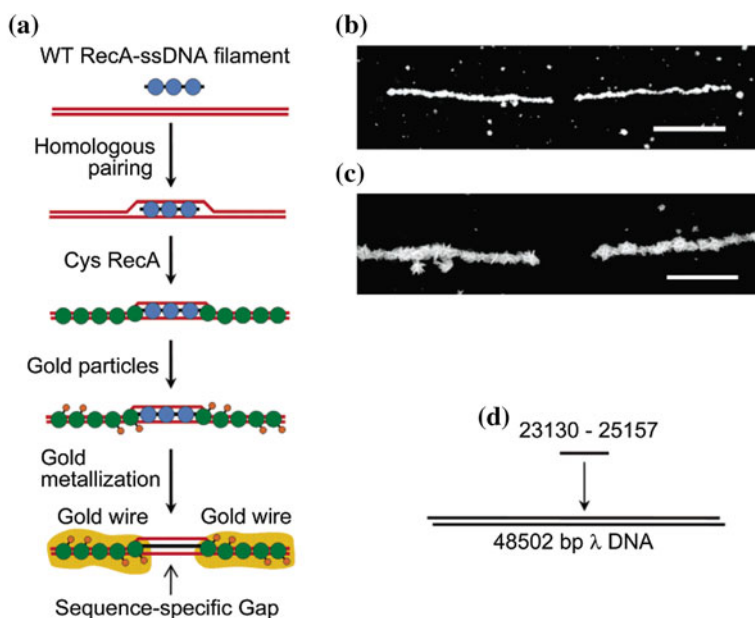


Fig. 6 Synthesis of conductive metal nanowires with a sequence-selective gap from complexes of single- or double-strand DNA and RecA protein. *Blue-* and *green-filled circles* indicate WT RecA and Cys RecA, respectively. The schema **a** shows how sequence selectivity is achieved: (i) Firstly, the wild-type RecA protein complexes with a copy of target ssDNA strand to be protected against metallization. Secondly, homologous pairing takes place and WT RecA is inserted in the DNA strand. Thirdly, the so-obtained DNA is exposed to Cys RecA, bearing the Cys grafting for the gold nanoparticles. Then the gold nanoparticles are fixed onto the Cys RecA regions. Finally, the template-based gold particles were enlarged by chemical deposition to form uniformly metallized nanowires with the desired sequence-specific gap. **b** and **c** Show two scanning electron microscope images of two sequence-specific gaps at different magnifications. The scale bar is, respectively, 5 and 2 μ m. **d** Indicates schematically the location of the ssDNA in λ scaffold. Adapted from [22]

component in recombinational DNA repair pathways and homologous genetic recombination (in *Escherichia coli*) [47]. In vitro, RecA protein demonstrates to promote the pairing and exchange of complementary DNA strands in reactions [48]. The mechanism is as follows: RecA catalyzes the pairing of single-strand DNA (ssDNA) with complementary regions of double-strand DNA (dsDNA). The RecA monomers first polymerize to form a helical filament around ssDNA (Fig. 3a). Duplex DNA is then bonded to the polymer (see Fig. 3b). However, it is worth to precise that RecA could polymerize onto dsDNA strands, too [49]. Thus, in ‘in vitro’ experiments after the polymerization onto ssDNA (Fig. 3a), the excess of free RecA should be removed to prevent an unspecific and undesired binding of RecA onto dsDNA [50].

In the framework of DNA-directed assembly of nanodevices, the RecA particular features have been used to differentiate a part of the DNA strand to achieve a sequence-selective metallization process. Indeed, the targeted sequence can be perfectly identified by the RecA-polymerized ssDNA fragment as in Fig. 3b. Then, the complex between the RecA–ssDNA polymer and the complementary regions of dsDNA can act as a mask for the metallization process. More in detail, the first report on sequence-specific metallization [14] suggested that this complex avoids the Ag^+/Na^+ ion-exchange blocking the formation of the Ag seeds on the targeted sequence. Consequently, the successive gold metallization is sequence selective since it takes place only where the metal seeds are present (see Fig. 4).

In a successive work [19], the same team showed that similar sequence-specific nanolithography can also be achieved by sequence-specific patterning of the local reducing agent (the glutaraldehyde). This patterning was performed either by ligation between aldehyde-derivatized and -underivatized DNA molecules or by sequence-specific protection against aldehyde derivatization by the RecA protein (see Fig. 5). Then, the sequence-specific patterning of the reducing agent is reflected by the sequence-specific creation of silver metallization seeds and successive gold metallization.

The third report on selective metallization uses the homologous recombination properties of the RecA protein, too. Its originality is to employ a modified RecA to act as a “linking factor” for sequence-specific fixation of gold nanoparticles [22]. Then, these gold nanoparticles are used as “seeds” for the metallization process. To be more precise, the authors use a genetically engineered cysteine derivative RecA protein (Cys-RecA) and, thanks to this derivatization, they are able to fix gold nanoparticles onto the Cys-RecA-DNA filament. Thus, they used separately cysteine-derivatized RecA and unmodified wild-type RecA (WT RecA) to complex different sequences of the DNA strand. Then, the fixation of the gold nanoparticles respects the targeted sequences bearing Cys-RecA-DNA and the successive metallization presents a sequence-specific gap corresponding to the unmodified RecA-DNA complex (see Fig. 6).

Finally, it is worth to say that also the method developed by the Carell group [26–29] could lead to sequence-selective conductive metallic nanowires since the metal seeds can be inserted onto a specific part of the sequences via the base labeling.

5 Applications of DNA Metallization in Nanoelectronics

In 2003, the Sivan group demonstrated the feasibility of DNA-directed approach for the assembling of a carbon nanotube field effect transistor [51]. In this work, some of the crucial ingredients of the DNA-directed vision were tackled and demonstrated, even if in a very simple and minimal geometry. More, in particular, the authors employed: (a) a selective placement of the nanotube on the DNA scaffold and (b) a sequence-selective metallization of the DNA strands. In this way, they were able to realize the electrical connection between the standard (lithographically defined) electrodes and the nanotube device. In both tasks (a) and (b), they exploited the sequence-specific homologous recombination of the RecA protein. They first anchored the single-wall carbon nanotube (SWNT) in the desired part of the DNA scaffold and then, after deposition on a substrate, proceeded to the selective metallization process. The SWNT/DNA linkage was performed in buffered solution by the molecular recognition of a streptavidin-functionalized SWNT toward biotin and by the antibodies' properties to link the biotin to the RecA/DNA filament, as schematized in Fig. 7.

Then, to fabricate the nanotube device, they stretched the SWNT/RecA/DNA assembly on a silicon substrate and performed the selective Ag/Au metallization process as described in Ref. [18]. One of the interesting features of this experiment is that even in this complicated configuration (presence of the SWNT, Streptavidin, biotin and antibodies species), the masking properties of the RecA are preserved and the "protected" segment of the DNA strand is not metallized. Finally, the DNA templated gold wires were connected by standard lithography electrodes to record the device characteristic. We note that DNA/RecA/SWNT complexes are randomly deposited on the silicon substrate and that the latter is also used as backgate. This implies that to fabricate the connecting electrodes, the deposited SWNT/RecA/DNA complex must be localized by imaging (AFM or SEM).

More recently, another approach has been proposed to fabricate a DNA-directed nanoelectrical device. In the report of the Winfree group [52], a DNA origami has been used as a nanobreadboard for arranging SWNTs as schematized in Fig. 8. Here, for device demonstration, the two SWNTs themselves ensure the electrical connections to the standard lithographically defined electrodes. More in detail, SWNTs were labeled by ssDNA to hybridize with hooks placed onto the origami. However, as already mentioned, when ssDNA spontaneously wrap around SWNTs, this ssDNA sequence is not readily available for the DNA-driven assembly. Thus, the authors used a particular engineered DNA fragment with a single-strand portion to wrap the SWNTs (the 40-T dispersal domain in Fig. 8a), while the part devoted to the hybridization is majorly dsDNA like with a 5bps LNA toehold in 3' (see Fig. 8a). The role of such LNA toehold is to initiate hybridization with origami hooks inducing the successive 15-bps ssDNA strand displacement. The authors reported that using DNA toehold instead of LNA, one decreases dramatically the yield of the reaction.

In this way, the authors [52] managed to align ssDNA-labeled SWNTs along the lines of complementary hooks onto origami. Crossed SWNT geometries were

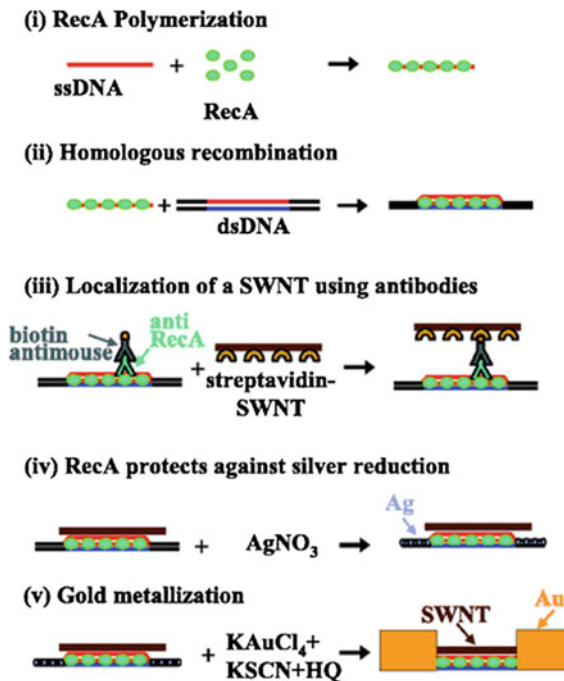


Fig. 7 Assembly of a DNA-templated FET and wires contacting it. Steps are as follows: (i) RecA monomers polymerize on a ssDNA molecule to form a nucleoprotein filament. (ii) Homologous recombination reaction leads to binding of the nucleoprotein filament at the desired address on an aldehyde-derivatized scaffold dsDNA molecule. (iii) The DNA-bound RecA is used to localize a streptavidin-functionalized SWNT, utilizing a primary antibody to RecA and a biotin-conjugated secondary antibody. (iv) Incubation in an AgNO₃ solution leads to the formation of silver clusters on the segments that are unprotected by RecA. (v) Electroless gold deposition, using the silver clusters as nucleation centers, results in the formation of two DNA-templated gold wires contacting the SWNT bound at the gap. Extracted from Ref. [51]

realized. In particular, their objective was to gate a semiconducting SWNT by a metallic SWNT using the DNA material present in the junction as gate dielectric. Indeed, by construction, the SWNTs are wrapped by ssDNA and the breadboard is also engineered to host the SWNT on different sides (see Fig. 8c).

If some criticisms are to be mentioned concerning this elegant work, they could be related to (i) the size of the DNA scaffolds with respect to the nanoobjects that are to be organized and (ii) the use of inter-SWNT DNA as gate dielectric material. Concerning the first point, the choice of arranging several hundred nanometers of SWNTs is probably dictated by the will of connecting these SWNTs by standard e-beam lithography and it is not very important since other scaffolds could be envisioned. In addition, this type of configuration could be of interest for relative positioning of nanoobject at the nanoscale and that longer objects like SWNTs could serve as wiring with larger electrical connexions. This type of approach has also been proposed by the group of Torma [53]. More specifically, Eskelinen et al.

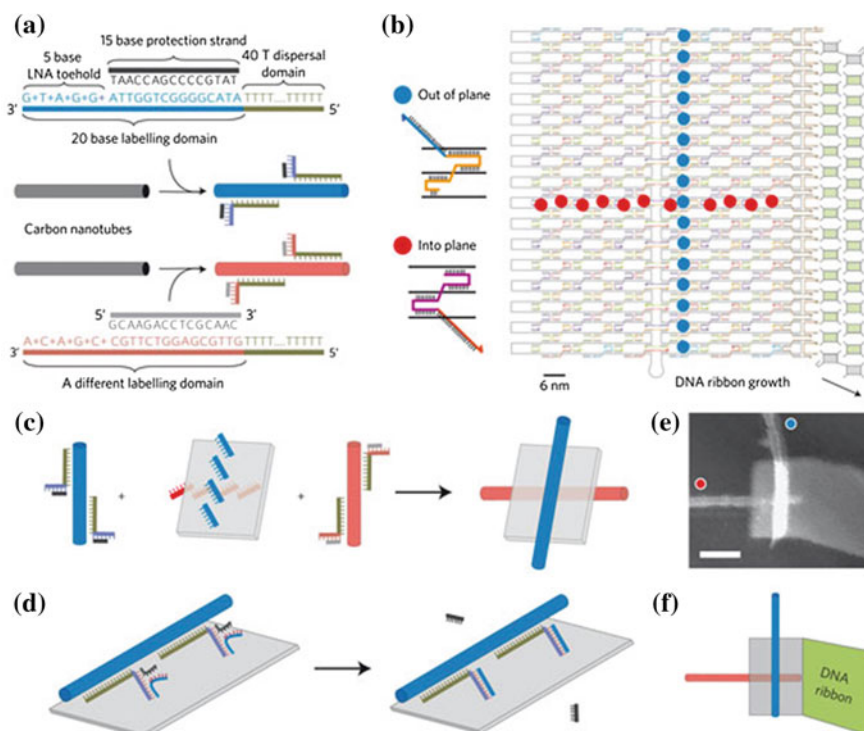


Fig. 8 Overview of cross-junction assembly. **a** ssDNA/SWNTs hybrids differ by linkers for which the labelling domains have different sequences. To distinguish them, SWNTs labeled with one sequence have been colored *red* and those labeled with the other, *blue*. Dispersal domains bind linkers to SWNTs; labeling domains project into solution. **b** A 7-kb-long scaffold strand (grey) and ssDNA staples (multicolored) form a rectangular origami template. Adapter strands (brown) on the right edge of the origami serve as nucleation sites for growth of a DNA ribbon (green/grey tiles). Red and blue dots indicate a pattern of hooks projecting from the origami. The insets show how staples are modified to carry hooks complementary to ssDNA/SWNT labeling domains of corresponding color; the scaffold is black. Red hooks project into the plane; blue hooks project out. **c** Red and blue ssDNA/SWNTs are mixed with a DNA template. They self-assemble sequence specifically with programmed orientations, red ssDNA/SWNTs horizontally and blue ssDNA/SWNTs vertically. **d** The toehold on a linker initiates binding to a hook, leading to branch migration and release of the protection strand. Ribbons are not shown in c and d. **e** A typical AFM height image of a cross-junction on mica under buffer; red and blue dots indicate ssDNA/SWNT type. Scale bar, 50 nm. **f** Schematic interpretation of e highlighting the relationship of origami, ribbon, and SWNTs. Extracted from Ref. [52]

[53] reported a similar (but simpler) method based on streptavidin–biotin recognition as schematized in Fig. 9.

In the work of Eskelinen et al., first biotins are fixed both on the SWNTs and on the origami via biotinylated-ssDNA (respectively, via origami design and thanks to the ssDNA wrapping around the SWNTs, as shown in Fig. 9a, c). Then, streptavidin is linked via the biotins onto the origami (Fig. 9b) and serves as docking points for the biotin-coated SWNTs (Fig. 9d).

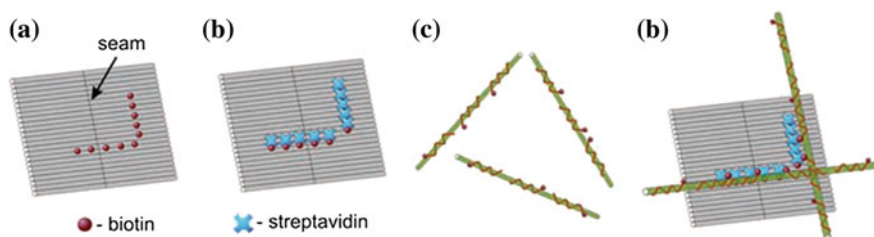


Fig. 9 Schematic diagram of CNT assembly on DNA origami templates using STV–biotin interaction. **a** As the first step, DNA origami structures with a certain pattern of biotin modifications were fabricated. **b** After that, streptavidin was assembled on the origami structure to define the binding sites for CNT attachment. Finally, **c** CNTs wrapped with biotin-modified ssDNA **d** were immobilized on the origami templates. Extracted from Ref. [53]

The main difference in these two reports is that in Maune’s approach [52], it is possible to choose different sequences of the “hook” onto the origami. Thus, it is possible to assemble different kinds of nano-objects using different sequences. On the contrary, in the method presented by Eskelinen [53], the linkage is ensured by streptavidin–biotin recognition and another kind of linkage should be found if it is necessary to relatively position different nanoobjects.

6 Conclusion

The demonstration of completely DNA-directed self-assembled circuits is, at the time of writing this overview, still to be done. The knowledge and mastering of the different steps needed for the implementation of such a demonstrator are already reported in the literature and it is now a matter of multidisciplinary will and teams to accomplish the task. Finally, for such a still open and exploratory research domain, new findings are expected to further enlarge the present vision and generate novel strategies for the long-term development of nanoelectronics.

References

1. International Technology Roadmap for Semiconductors (ITRS): <http://www.itrs.net>
2. Seeman, N.C.: Nature **421**, 427 (2003)
3. Seeman, N.C.: The use of branched DNA for nanoscale fabrication. Nanotechnology **2**, 149 (1991)
4. Alivisatos, A.P., Johnsson, K.P., Peng, X.G., Wilson, T.E., Loweth, C.J., Bruchez, M.P., Schultz, P.G.: Organization of ‘nanocrystal molecules’ using DNA. Nature **382**, 609 (1996)
5. Niemeyer, C., Ceyhan, B.: DNA-directed functionalization of colloidal gold with proteins. Angew. Chem. Int. Ed. **40**, 3685 (2001)
6. Mirkin, C.A.: Programming the assembly of two- and three-dimensional architectures with DNA and nanoscale inorganic building blocks. Inorg. Chem. **39**, 2258 (2000)

7. Li, H., Park, S.A., Reif, J.H., LaBean, T.H., Yan, H.: DNA-templated self-assembly of protein and nanoparticle linear arrays. *J. Am. Chem. Soc.* **126**, 418 (2004)
8. Hollenberg, C.P., Di Mauro, E.: "DNA and DNA technology for the construction of networks to be used in chip construction and chip production (DNA-chips)". US Patent 5,561,071 (1996)
9. de Pablo, P.J., Moreno-Herrero, F., Colchero, J., Gomez Herrero, J., Herrero, P., Bar, A.M., Ordejon, P., Soler, J.M., Artacho, E.: Absence of dc-Conductivity in λ -DNA. *Phys. Rev. Lett.* **85**, 4992 (2000)
10. Storm, A.J., Van Noort, J., de Vries, S.J., Dekker, C.: Insulating behavior for DNA molecules between nanoelectrodes at the 100 nm length scale. *Appl. Phys. Lett.* **79**, 3881 (2001)
11. Zang, Y., Austin, R.H., Kraeft, J., Cox, E.C., Ong, N.P.: Insulating behavior of λ -DNA on the micron scale. *Phys. Rev. Lett.* **89**, 198102 (2002)
12. Tuukkanen, S., Kuzyk, A., Toppari, J.J., Hytönen, V.P., Ihalainen, T., Törmä, P.: Dielectrophoresis of nanoscale double-stranded DNA and humidity effects on its electrical conductivity. *Appl. Phys. Lett.* **87**, 183102 (2005)
13. Braun, E., Eichen, Y., Sivan, U., Ben-Joseph, G.: DNA-templated assembly and electrode attachment of a conducting silver wire. *Nature* **391**, 775 (1998)
14. Siedel, R., Colombi Ciacchi, L., Weigel, M., Pompe, W., Mertig, M.J.: Synthesis of platinum cluster chains on DNA templates: conditions for a template-controlled cluster growth. *Phys. Chem. B* **108**, 10801 (2004)
15. Richter, J., Seidel, R., Kirsch, R., Mertig, M., Pompe, W., Plaschke, J., Schackert, H.K.: Nanoscale palladium metallization of DNA. *Adv. Mater.* **12**, 507 (2000)
16. Seidel, R., Mertig, M., Pompe, W.: Scanning force microscopy of DNA metallization. *Surf. Int. Anal.* **33**, 151 (2002)
17. Ford, W.E., Harnack, O., Yasuda, A., Wessels, J.M.: Platinated DNA as precursors to templated chains of metal nanoparticles. *Adv. Mat.* **13**, 1793 (2001)
18. Keren, K., Krueger, M., Gilad, R., Ben-Joseph, G., Sivan, U., Braun, E.: Sequence-specific molecular lithography on single DNA molecules. *Science* **297**, 72 (2002)
19. Keren, K., Berman, R., Braun, E.: Patterned DNA metallization by sequence-specific localization of a reducing agent. *Nanoletters* **4**, 323 (2004)
20. Richter, J.: Metallization of DNA. *Physica E* **16**, 157 (2003)
21. Harnack, O., Ford, W.E., Yasuda, A., Wessels, J.: Tris(hydroxymethyl)phosphine-Capped gold particles templated by DNA as nanowire precursors. *Nanoletters* **2**, 919 (2002)
22. Nishinaka, T., Takano, A., Doi, Y., Hashimoto, M., Nakamura, A., Matsushita, Y., Kumaki, J., Yashima, E.: Conductive metal nanowires templated by the nucleoprotein filaments, complex of DNA and RecA protein. *J. Am. Chem. Soc.* **127**, 8120 (2005)
23. Ongaro, A., Griffin, F., Beecher, P., Nagle, L., Iacopino, D., Quinn, A., Redmond, G., Fitzmaurice, D.: DNA-templated assembly of conducting gold nanowires between gold electrodes on a silicon oxide substrate. *Chem. Matter.* **17**, 1959 (2005)
24. Ahernel, D., Satti, A., Fitzmaurice, D.: Diameter-dependent evolution of failure current density of highly conducting DNA-templated gold nanowires. *Nanotechnology* **18**, 125205 (2007)
25. Nakao, H., Shiigi, H., Yamamoto, Y., Tokonami, S., Nagaoka, T., Sugiyama, S., Ohtani, T.: Highly ordered assemblies of Au nanoparticles organized on DNA. *Nanoletters* **3**, 1391 (2003)
26. Burley, G.A., Gierlich, J., Mofid, M.R., Nir, H., Tal, S., Eichen, Y., Carell, T.J.: Directed DNA metallization. *Am. Chem. Soc.* **128**, 1398–1399 (2006)
27. Fischler, M., Simon, U., Nir, H., Eichen, Y., Burley, G.A., Gierlich, J., Gramlich, P.M.E., Carell, T.: Formation of bimetallic Ag–Au nanowires by metallization of artificial DNA duplexes. *Small* **3**, 1049 (2007)
28. Timper, J., Gutmiedl, K., Wirges, C., Broda, J., Noyong, M., Mayer, J., Carell, T., Simon, U.: Surface "click" reaction of DNA followed by directed metalization for the construction of contactable conducting nanostructures. *Angew. Chem. Int. Ed.* **51**, 7586 (2012)
29. Fischler, M., Sologubenko, A., Mayer, J., Clever, G., Burley, G., Gierlich, J., Carell, T., Simon, U.: Chain-like assembly of gold nanoparticles on artificial DNA templates via 'click chemistry'. *Chem. Comm.* **169** (2008)

30. Gold enhancement as performed by Carell group : A solution of KSCN (0.5 mL, 60 mg mL⁻¹) was mixed with a solution of KAuCl₄ (0.5 mL, 23 mg mL⁻¹). The mixture was centrifuged at 2000 rpm for 1 min and the orange precipitate was separated from the supernatant. The precipitate was dissolved in phosphate buffer (8 mL, 0.05M, pH 5) and added to a solution of hydroquinone (250 µL, 5.5 mg mL⁻¹) immediately before the metallization process. US Patent 5,561,071
31. <http://www.nanoprobe.com/pdf/Inf2113.pdf>
32. Yan, H., Park, S.H., Finkelstein, G., Reif, J.H., LaBean, T.H.: DNA-templated self-assembly of protein arrays and highly conductive nanowires. *Science* **301**, 1882 (2003)
33. Monsoon, C.F., Woolley, A.T.: DNA-templated construction of copper nanowires. *Nanoletters* **3**, 359 (2003)
34. Swami, A.S., Brun, N., Langevin, D.: Phase transfer of gold metallized DNA. *J. Clust. Sci.* **20**, 281 (2009)
35. Dupraz, C.J.-F., Nickels, P., Beierlein, U., Huynh, W.U., Simmel, F.C.: Towards molecular scale electronics and biomolecular self-assembly. *Superlattices Microstruct.* **33**, 369–379 (2003)
36. Lippert, B. (ed.): *Cisplatin: Chemistry and Biochemistry of a Leading Anticancer Drug*. Wiley-VCH, Weinheim, Germany (1999)
37. Macquet, J.P., Theophanides, T.: Spécificité de l'interaction DNA-platine dosage du platine, pH métrie. *Biopolymers* **14**, 781–799 (1975)
38. Colombi Ciacchi, L., Mertig, M., Seidel, R., Pompe, W., de Vita, A.: Nucleation of platinum clusters on biopolymers: a first principles study of the molecular mechanisms. *Nanotechnology* **14**, 840–848 (2003)
39. Macquet, J.P., Theophanides, T.: DNA-platinum interactions. Characterization of solid DNA/K₂PtCl₄ complexes. *Inorg. Chim. Acta* **18**, 189–194 (1976)
40. Macquet, J.P., Butour, J.L.: A circular dichroism study of DNA-platinum complexes. *Eur. J. Biochem.* **83**, 375–385 (1978)
41. Berti, L., Alessandrini, A., Facci, P.: DNA-templated photoinduced silver deposition. *J. Am. Chem. Soc.* **127**, 11216–11217 (2005)
42. Mertig, M., Colombi Ciacchi, L., Seidel, R., Pompe, W., De Vita, A.: DNA as a selective metallization template. *Nanoletters* **2**, 841–844 (2002)
43. Richter, J., Mertig, M., Pompe, W., Monch, I., Schackert, H.K.: Construction of highly conductive nanowires on a DNA template. *Appl. Phys. Lett.* **78**, 536–538 (2001)
44. Nguyen, K., Streiff, S., Lyonnais, S., Goux-Capes, L., Goffman, M., Bourgoin, J.P., Filoramo, A.: DNA-based nanoscale integration: aip conference proceedings, **859**, pp. 39-44 (2006)
45. Deng, Z., Mao, C.: DNA-templated fabrication of 1D parallel and 2D crossed metallic nanowire arrays. *Nano Lett.* **3**, 1545–1548 (2003)
46. Nguyen, K., Monteverde, M., Filoramo, A., Goux-Capes, L., Lyonnais, S., Jegou, P., Viel, P., Goffman, M., Bourgoin, J.P.: Synthesis of thin and highly conductive DNA-based palladium nanowires. *Adv. Mater.* **20**, 1099 (2008)
47. Roca, Alberto I., Cox, Michael M.: RecA protein: structure, function, and role in recombinational DNA repair. *Prog. Nucleic Acid Res. Mol. Biol.* **56**, 129–223 (1997)
48. Cox, M.M.: Alignment of 3 (but Not 4) DNA strands within a RecA protein filament. *J. Biol. Chem.* **270**, 26021 (1995)
49. Leger, J.F., Robert, J., Bourfieu, L., Chatenay, D., Marko, J.F.: RecA binding to a single double-stranded DNA molecule: A possible role of DNA conformational fluctuations. *PNAS* **95**, 12295 (1998)
50. Szybalski, W.: RecA-mediated Achilles' heel cleavage. *Curr. Opin. Biotechnol.* **8**, 75 (1997)
51. Keren, K., Berman, R.S., Buchstab, E., Sivan, U., Braun, E.: DNA-templated carbon nanotube field-effect transistor. *Science* **302**, 1380–1382 (2003)
52. Maune, H.T., Han, S.-P., Barish, R.D., Bockrath, M., Goddard III, W.A., Rothmund, P.W.K., Winfree, E.: Self-assembly of carbon nanotubes into two-dimensional geometries using DNA origami templates. *Nat. Nanotechnol.* **5**, 61–66 (2009)
53. Eskelinen, A.P., Kuzy, A., Kaltiaisenaho, T.K., Timmermans, M.Y., Nasibulin, A.G., Kauppinen, E.I., Törmä, P.: Assembly of single-walled carbon nanotubes on DNA-origami templates through streptavidin–biotin interaction. *Small* **7**, 746 (2001)

Nanopackaging: From Nanomaterials to the Atomic Scale

Proceedings of the 1st International Workshop on Nanopackaging, Grenoble 27-28 June 2013

Baillin, X.; Joachim, C.; Poupon, G. (Eds.)

2015, VIII, 189 p. 124 illus., 47 illus. in color., Hardcover

ISBN: 978-3-319-21193-0